

Preparation and electrochemical properties of pitch-based carbon foam as current collectors for lead acid batteries

Ya Chen^{*}, Bai-Zhen Chen, Xi-Chang Shi, Hui Xu,
Wei Shang, Yan Yuan, Lu-Ping Xiao

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

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Abstract

Pitch-based carbon foam with large pore size in the cell walls was prepared and evaluated as possible current collectors of lead acid batteries. Cyclic voltammetry and galvanostatic charge–discharge experiments were performed on the material to evaluate its electrochemical properties. The carbon foam is electrochemically stable in the voltage range where the negative electrodes of lead acid batteries operate, while oxygen evolution at the foam occurs below the voltage related to the oxidation of PbSO_4 to PbO_2 . Initial charge–discharge characterization of the carbon foam coated with lead oxide pastes shows that the carbon foam is suitable for use as negative current collectors of lead acid batteries, but cannot be used as positive current collectors due to the oxygen evolution. To use the carbon foam as positive current collectors, further study is necessary to increase the overpotential for the oxygen evolution.

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1. Introduction

Lead acid battery has been used widely for more than 100 years since its invention by Planté in 1859 [1,2]. Although various newer batteries, including lithium, lithium ion, and nickel metal hydride batteries, exhibit much higher energy densities than lead acid batteries, advanced lead acid batteries are still the most important rechargeable electrochemical storage system today. Conventional lead acid batteries are relatively heavy and thus have low specific energy due to the use of heavy lead alloy grids as the current collector materials [3]. To improve the specific energy, lightweight, electronically conductive materials have been widely investigated as the potential substitutes for lead alloy grids [4–6]. Carbon foams attracted much attention and emerged as current collector materials of great promise due to their specific properties, such as lightweight, large specific surface, good corrosion resistance, and high electrical conductivity [6–9]. While reticulated vitreous carbon (RVC), an open-pore

foam of glass-like carbon, was investigated as current collector more than 10 years ago, the lead acid batteries using RVC as current collectors are still at the development stage. Low stiffness and strength of RVC may be the main limiting factors in their commercial application.

Recently, pitch-based graphite foam with high strength and thermal conductivity was developed by researchers at Oak Ridge National Laboratory [10]. The electrochemical stability of the foam as current collectors for lead acid batteries has also been evaluated by Jang et al. [9]. Unfortunately, the results showed that the foam was not electrochemically stable in the voltage range of positive electrode, and it was difficult to uniformly apply the battery pastes on the foam due to the small windows in the cell walls. Furthermore, the high production cost of the carbon foam may also limit their use as current collectors for lead acid batteries. In this paper, to develop carbon foam suitable for use as current collectors in lead acid batteries, pitch-based carbon foam with large pore size in the cell walls was fabricated by a template method, and the electrochemical properties of the foam as current collectors for lead acid batteries were characterized by cyclic voltammetry and galvanostatic charge–discharge tests.

^{*} Corresponding author. Tel.: +86 731 8877352; fax: +86 731 8877171.
E-mail address: chenya1973a@sina.com (Y. Chen).

2. Experimental

The carbon foam was prepared by a template method. A petroleum-derived pitch (Zaoqing Chemical Plant, Guangdong, China) with high softening point was selected as the precursor and a polyurethane foam with pore size of 25 ppi (pores per inch) as the template material. The pitch was ground and mixed with 2% by weight of organic additives (binder, thickener and suspension agent) and 35% by weight of distilled water to form homogeneous slurry. Into this slurry at room temperature polyurethane foam slabs with dimensions of 50 mm × 30 mm × 6 mm were dipped for 3 min to impregnate. The impregnated polyurethane foam slabs were then passed between pair of rollers to adjust the distribution and amount of slurry present on the slabs. The polyurethane foam slabs coated with water-pitch slurry were dried, and then heated to 450 °C in nitrogen and soaked for 2 h to form “interparticulate bonded” pitch foam. After cooling, the obtained pitch foam slabs were oxidized at 0.1 °C min⁻¹ up to 350 °C in an air flow of 0.8 m³ h⁻¹, and then carbonized at 1000 °C for 3 h in a high purity argon flow. The microstructure of the obtained carbon foam was observed under a JSM-6360 LV scanning electron microscope (SEM). The surface area was measured by nitrogen adsorption and desorption method using a JW-K adsorption system. The conductivity and bulk density were determined by four-point measurement and weighing, respectively.

The carbon foam slabs used for electrochemical tests were connected with conductive wires by soldering, and the joints were coated with epoxy resin. Cycle voltammetry was performed at a scan rate of 5 mV s⁻¹ using a CHI660B electrochemical workstation and a three-electrode beaker cell. In all case, the reference electrode was Hg/Hg₂SO₄ in saturated K₂SO₄ solution (MSE), and 50 ml of 4.5 M H₂SO₄ solution was used as the electrolyte. The counter electrode was large piece of lead. The carbon foam slab as the working electrode was covered with epoxy resin with dimensions of circa (ca.) 25 mm × 6 mm × 5 mm exposed on one top (the welding joint was on the other top), thanks to the carbon foam slabs have high surface area which may influence the test results. For comparison, the electrochemical characterization was also performed on a lead piece with a geometric area of ca. 2 cm² immersed in the electrolyte.

The battery paste was prepared by a common method described in Ref. [11]. The lead oxide powder containing 75% by weight of lead oxide and 25% by weight of metallic lead were used as the raw material for both positive and negative electrode. The lead oxide powder (50 g) was combined with sulfuric acid (6 ml of 14.5% solution) and distilled water (12 ml) to make the positive electrode paste. To prepare the negative electrode paste, lead oxide powder (50 g), distilled water (7 ml), barium sulfate powder (0.5 g), and lignosulfonate (0.5 g) were mixed for 10 min, then sulfuric acid (6 ml of 14.5% solution) was added to the mixture and mixed for another 10 min. The pastes were physically forced into the pores of the carbon foam slabs with a plastic spatula, and excess pastes were scraped off of the surface. Subsequently, the coated foam slabs were immersed in diluted sulfuric acid (14.5% solution) for about 5 s, and then cured at

70 °C and a relatively humidity 90% for 36 h, and dried at 80 °C for 12 h.

The amount of active material coated on the foam slab used as negative current collector was ca. 0.4 g, and the electrode size (dimensions of coated part of the foam slab) was ca. 25 mm × 6 mm × 2 mm. The loading of active material per gram of the foam current collector was ca. 4.5 g. For the positive electrode, the amount of active material and electrode size were ca. 0.8 g and ca. 25 mm × 12 mm × 2 mm, respectively. The uncoated part of the foam (for both positive and negative electrodes) was coated with epoxy resin. For comparison, a positive electrode using a lead piece as the current collector was also prepared by the same method. The electrode size and amount of active material were ca. 25 mm × 12 mm × 3 mm and ca. 1 g, respectively.

With the prepared electrodes, flooded cells were assembled, and galvanostatic charge–discharge tests were performed using a Newware battery test system. Each cell has one positive electrode and one negative electrode, thus the charge–discharge capacity was limited by the negative electrode. The cells were charged to 2.4 V at 0.05 C (20 h rate) and then charged to 2.57 V at 0.025 C, followed by their discharge at 0.05 C. The discharge cut-off voltage was 1.7 V. H₂SO₄ solution (50 ml of 4.5 M) was used as the electrolyte for the galvanostatic charge–discharge tests.

3. Results and discussion

The photograph and SEM image of the carbon foam are presented in Figs. 1 and 2, respectively. After carbonization, although the measured shrinkage is up to about 15% along each



Fig. 1. Photograph of the carbon foam.

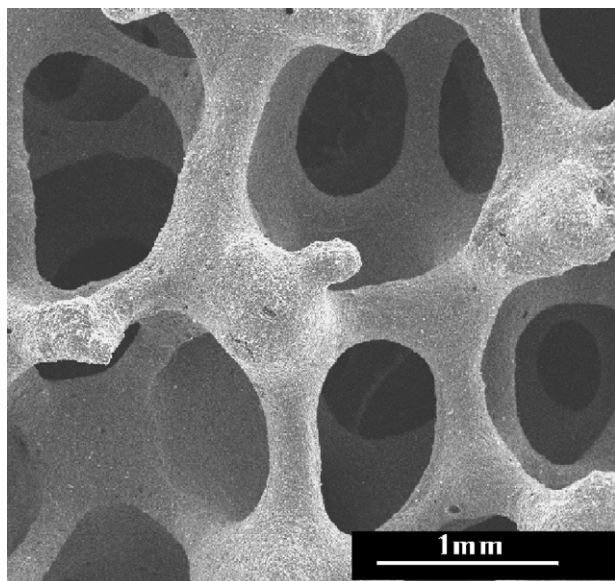


Fig. 2. SEM images of carbon foam.

side of the slabs, the pore structure of the foam is preserved well. The cells are still open and uniform. More important, the large pore size in the cell walls can ensure homogeneous distribution of the electrode pastes throughout the foam. The bulk density and surface area of the carbon foams are 0.3 g cm^{-3} and $89 \text{ cm}^2 \text{ cm}^{-3}$, respectively. The bulk conductivity is up to 20 S cm^{-1} . One of the carbon foam slabs was cut and the cross-section of the ligaments was observed under a reading glass. It was found that the polyurethane used as the template has become part of the foam material which is much darker than the pitch-based carbon.

Fig. 3 shows the typical cyclic voltammograms (CVs) of metallic lead. Fig. 3a shows the CV of the metallic lead between 0 and -1.8 V . The main redox processes of the lead electrode indicated by peaks A–C are: (A) H_2 evolution; (B) $\text{PbSO}_4 \rightarrow \text{Pb}$; (C) $\text{Pb} \rightarrow \text{PbSO}_4$. Fig. 3b shows the CV of the electrode between 0 and 1.8 V . The peak E is related to $\text{PbO}_2 \rightarrow \text{PbSO}_4$, while peak F corresponds to $\text{PbSO}_4 \rightarrow \text{PbO}_2$ and O_2 evolution. The reduction of PbO_2 to PbSO_4 at peak E is accompanied by a large increase of the molar volume. As a result, the sulfate layer cracks, exposing bare metallic lead to H_2SO_4 solution. The small oxidation peak D (shown in the inset) observed after the main reduction peak E is due to the oxidation of the freshly exposed Pb to PbSO_4 [9]. The peaks are related to half-cell reactions occurring in lead acid batteries during charge and discharge. The cathodic peak B and anodic peak C correspond to the negative electrode reactions, while the cathodic peak E and anodic peak F correspond to the positive electrode reactions. It can be clearly seen that the oxidation of PbSO_4 to PbO_2 (charge reaction) at the positive electrode of lead acid batteries occurs above 1.4 V . The peak potentials of the peaks B and C are 1.06 and 0.95 V , respectively.

Fig. 4 shows the CVs of a carbon foam-working electrode. Fig. 4a shows the CV of the foam electrode in the voltage range between -1.8 and 0 V . No current peak is observed in this voltage range except the onset of hydrogen evolution at ca. -1.2 V .

This indicates that the carbon foam is electrochemically stable in the voltage range between -1.2 and 0 V . The voltage range includes the operation voltage for the negative electrode of lead acid batteries. Since the redox reactions at the electrode occur above -1.2 V , as indicated by the peaks B and C in Fig. 3a, the carbon foam is promising as a negative current collector for lead acid batteries. Fig. 4b shows the CV of the foam electrode in the voltage range between 0 and 1.8 V . No peak is observed too, except the onset of oxygen evolution. But it is noteworthy that the onset of oxygen evolution occurs at ca. 0.6 V . Charge acceptance reflects the ratio between the discharge capacity and charge capacity of a battery [12]. Since the oxidation of PbSO_4 to PbO_2 occurs above 1.4 V at the positive electrode of lead acid batteries, the oxygen evolution at the carbon foam will lead to poor charge acceptance of the lead acid batteries using the foam material as positive current collectors.

Galvanostatic charge–discharge experiment was performed on a flooded cell. The positive and negative electrodes were carbon foam slabs coated with lead oxide pastes. Fig. 5 shows the charge–discharge curves. Although the cell was expected to be charged to 2.4 V at 0.05 C and then charged to 2.57 V at 0.025 C , the voltage could not reach to 2.4 V even after a long-time charge

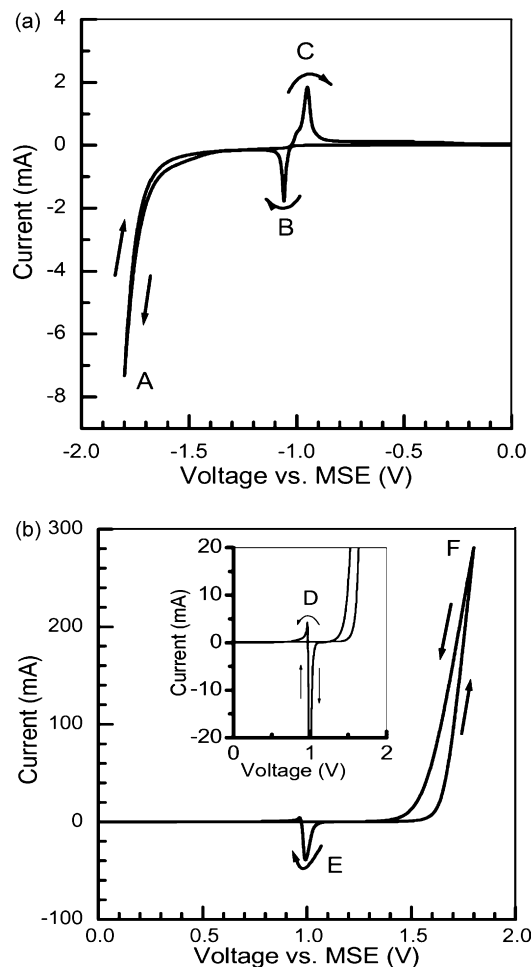


Fig. 3. Cyclic voltammograms of metallic lead between (a) -1.8 and 0 V , (b) 0 and 1.8 V vs. MSE in 4.5 M solution. The scan rate is 5 mV s^{-1} , and the electrolyte is $4.5 \text{ M H}_2\text{SO}_4$ solution.

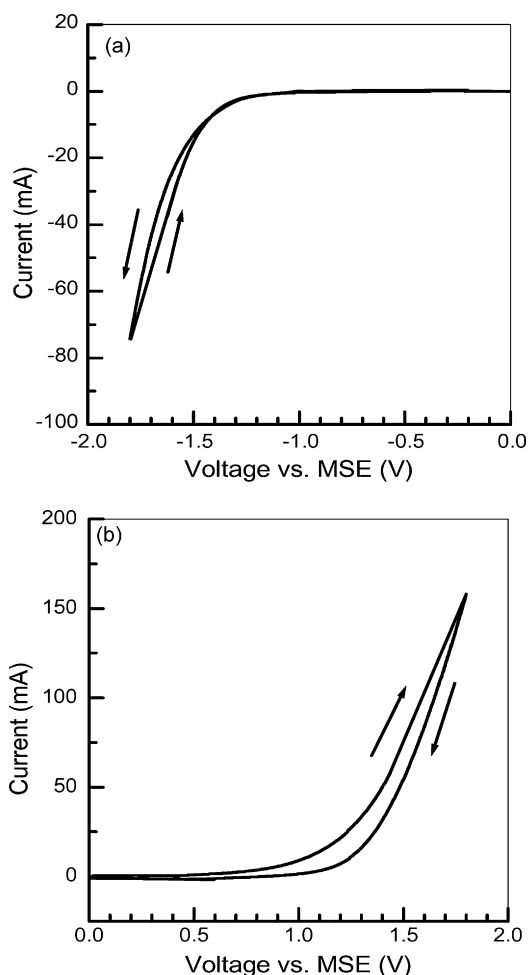


Fig. 4. Cyclic voltammograms of carbon foam between (a) -1.8 and 0 V, (b) 0 and 1.8 V vs. MSE in 4.5 M solution. The scan rate is 5 mV s^{-1} , and the electrolyte is $4.5 \text{ M H}_2\text{SO}_4$ solution.

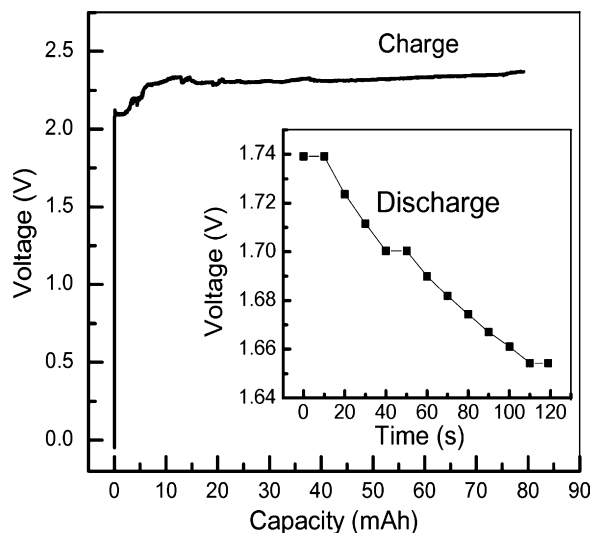


Fig. 5. The first charge–discharge curves of a cell. The positive and negative electrodes are carbon foams coated with lead oxide paste. The charge–discharge current is 4 mA .

process. On the other hand, number of gas bubbles were observed arising from the surface of the positive electrode after the voltage reached to about 2.0 V . The charge process was manually stopped after the charge capacity reached up to 80 mAh . The inset shows the first discharge curve of the cell. The voltage of the cell immediately dropped to 1.74 V after the charge was stopped, and rapidly dropped to below 1.7 V after the discharge began. This indicates that the cell using the carbon foam as both positive and negative current collectors has poor charge acceptance due to the oxygen evolution. The charge–discharge curves are consistent with the CVs in Fig. 4. When the electrodes were taken out of the cell after the charge–discharge testing, it was found that the active material coated on the positive current collector was badly loose due to the impact of oxygen evolution. To use the carbon foam as positive current collectors in lead acid batteries, surface modification of the foam material seems necessary to increase the overpotential for oxygen evolution.

For comparison, the charge–discharge experiment was again performed on a cell using a carbon foam slab as the negative current collector and a lead grid as the positive current collector. Fig. 6 shows the first charge–discharge curves. The cell exhibits an initial discharge capacity of 52 mAh . The utilization efficiency of the negative paste is ca. 60% and the charge acceptance reaches up to 72% . The cell was cycled for 20 cycles and the data are shown in Fig. 7. The cell attained its maximum capacity within the initial three cycles, and no clear capacity loss was observed within the 20 cycles. The cell capacity decreased rapidly beyond 20 cycles due to active material shedding from the positive electrode. But no obvious change was observed on the negative electrode and the active material was still tightly bound to the carbon foam. This suggests that the carbon foam can be used as negative current collectors for lead acid batteries. Nevertheless, further study is still needed to improve the cycle performance of the cell. Optimization of the positive paste formulation, improvement of the pasting and curing techniques, adoption of commercial lead alloy grids as the positive current collectors are expected to yield better cycle performance in the future.

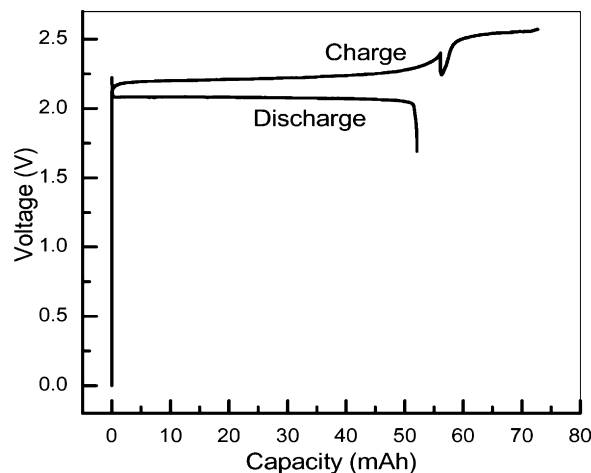


Fig. 6. The first charge–discharge curves of a cell. The positive and negative electrodes are lead grid and carbon foam coated with lead oxide paste, respectively. The charge–discharge current is 4 mA .

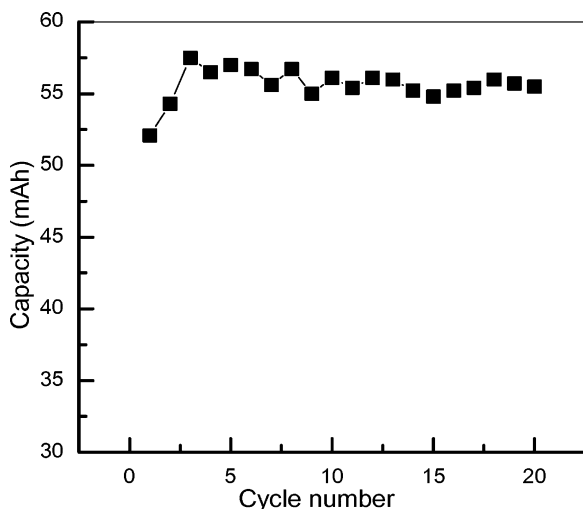


Fig. 7. Capacity as a function of cycle number of a cell. The positive and negative electrodes of the cell are lead grid and carbon foam coated with lead oxide paste, respectively. The charge–discharge current is 4 mA.

4. Conclusions

Pitch-based carbon foam prepared by a template method was evaluated as the current collectors of lead acid batteries. Cyclic voltammetry tests show that the carbon foam is electrochemically stable in the voltage range where the negative electrodes operate. However, O_2 evolution at the carbon foam occurs below the voltage related to the oxidation of $PbSO_4$ to PbO_2 . Initial charge–discharge characterization of the carbon foam coated

with lead oxide pastes shows that the carbon foam is suitable for use as negative current collectors of lead acid batteries, but cannot be used as positive current collectors due to the oxygen evolution. To use the carbon foam as positive current collectors, it is necessary to increase the overpotential for the oxygen evolution. Further study and evaluation are also needed for commercial exploitation of the carbon foam as negative current collectors in lead acid batteries.

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